Formation of Heneicosane-2,4-dione by Acid-Catalyzed Rearrangement of Isopropenyl Stearate

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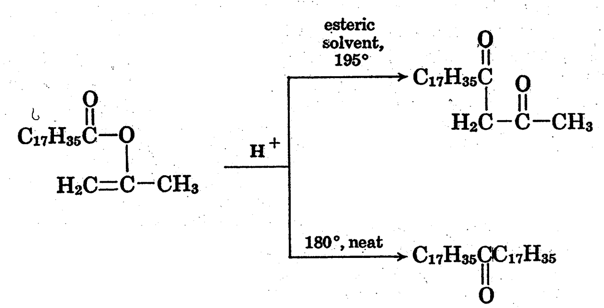
We have used the enol ester, isopropenyl stearate, as an effective stearoylating agent.[2] The sole by-product, acetone, is driven off as a gas, thereby driving reaction to completion. Since even so weakly protonic a substance as N-methylstearamide is stearoylatable by such a procedure, we considered that diethyl malonate should also stearoylate at the active methylene group on refluxing the reactants together in the presence of the usual trace of acid catalyst.



An anomalous crystalline reaction product having double melting points at 70 and 75° was obtained in 70% yield instead. Acetone, although evolved and collected, was formed in a molecular proportion of only about 10% of the expected value. At first we thought that the unexpected compound might be the O-acylation product, since the infrared spectrum showed carbonyl region bands at 1774, 1737 (intense), and 1644 cm^{-1}, the latter band presumed to be indicative of olefinic unsaturation. In accord with this, the substance was found to absorb strongly in the ultraviolet at 298 mμ. However, the elemental analysis precluded such a supposition and showed the product to be isomeric with isopropenyl stearate. The same isomeric product was also obtained when methyl stearate was used as the quasi-reactant instead of diethyl malonate, suggesting that all portions of the new molecule are constructed from isopropenyl stearate only.

From this and other data it is apparent that the product melting at 70 and 75° is the rearrangement product heneicosane-2,4-dione, $C_{17}H_{35}COCH_2COCH_3$. A search of the literature uncovered previous reports of such a rearrangement carried out pyrolytically at 500° on short-chain molecules.[3-5] Ultraviolet photochemical rearrangement of enol esters to β-diketones has also succeeded, but products obtained by photochemical change on a given substrate may be different from those obtained pyrolytically.[6] Feldkimel-Gorodetsky and Mazur have shown, for example, that 1-benzoyloxycyclohexene gives the ring-cleavage product, 1-benzoyl-5-hexen-2-one on irradiation, but gives 2-benzoylcyclohexanone on pyrolysis. Ritchie and Yousufzai[5] have presented evidence for a four-membered transitional cyclic compound, and Finnegan and Hagen[7] have shown a formal resemblance to the Fries rearrangement.

Since the "solvent" diethyl malonate or methyl stearate played no apparent role in the rearrangement, an experiment was carried out without solvent. By this means, we hoped to avoid the technical separation difficulties in removing high-boiling diethyl malonate and by-product ethyl stearate[8] formed by ester interchange. For this reason, isopropenyl stearate was held molten at 200° for 1 hr with a catalytic amount of p-toluenesulfonic acid in the expectation of obtaining heneicosane-2,4-dione in nearly pure form. Surprisingly, the β-diketone was, to the contrary, formed in only small amount, the major product being stearone, formed in high yield.

To exclude the dilution effect from consideration in accounting for the different products, we heated isopropenyl stearate with acid catalyst substituting a volume of Nujol, an inert high-boiling hydrocarbon, equal to that of the previously used diethyl malonate. Although acetone evolution did occur, no β-diketone at all formed in 20 min at 185° and only traces of β-diketone formed at 200° during 1-hr heating. In the former case, unchanged starting material and an unknown substance absorbing at about 1815 cm^{-1} were found. At the higher temperature and longer reaction time, the starting isopropenyl stearate was completely consumed, but only trivial amounts of heneicosanedione and stearone were formed, together with increased amounts of the 1815-cm^{-1} absorbing substance which appears not to be an anhydride. In view of the three different results in the three different media, the solvent effect cannot be ignored.

A reviewer has called our attention to the wide deviation of the infrared and ultraviolet absorption data of our heneicosane-2,4-dione, $\bar{\nu}_{max}^{CS_2}$ 1737 cm^{-1}, $\lambda_{max}^{isooctane}$ 298 mμ (ϵ 3000), from that of acetylacetone which absorbs 1530 to 1640 cm^{-1} (broad) with a weaker band at 1709 cm^{-1} and exhibits λ_{max} 271 mμ. This apparent discrepancy merely reflects the existence of tautomeric forms. Acetylacetone exists principally in the chelated-ring, monoenolic form while our fatty acid compound apparently exists mainly in the β-diketonic tautomeric form. The band differences have been used by previous workers in measuring the

(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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(5) P. D. Ritchie and A. H. K. Yousufzai, *Chem. Ind.* (London), 1918 (1964).

(6) M. Feldkimel-Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

(7) R. A. Finnegan, and A. W. Hagen, *Tetrahedron Letters*, 365 (1963).

(8) R. L. Adelman [*J. Org. Chem.*, **14**, 1057 (1949)] reported ester interchange in vinyl and isopropenyl esters as being highly unusual.

degree of enolization of β-diketones. Eistert and Reiss[9] report for benzoylcamphor a band at 247 mμ (ϵ 14,900) for the enol chelate tautomer and 309 mμ (ϵ 7800) for the diketo tautomer. Dimedon[10] absorbs at 1702 and 1724 cm^{-1} (weak), showing the presence of β-diketonic tautomer, and Kirmann and Wakselman[11] give 1500–1650 cm^{-1} (strong) and $\lambda_{max}^{dioxane}$ 275 mμ (ϵ 13,950) for large-ring, cyclic β-diketones but 1650 (weak) and 1700 cm^{-1} (strong) for similar compounds bearing a single methyl substituent on the carbon atom between the two carbonyl groups (decreased enolization). The compound 2-acetylcyclohexanone in hexane absorbs at 288 mμ (ϵ 6900), and Nakanishi[12] reports (no references) $\bar{\nu}_{max}$ 1720 (occasionally a doublet) for β-diketones. In view of the fact that long-chain β-diketones are not previously reported in the literature, there is no reason to doubt the present values but rather to conclude that one has essentially the β-diketo tautomer in hand. The "extra" peak[12] in the infrared spectrum at 1774 cm^{-1} probably reflects the ketone ketone interaction just as the two equal carbonyl groups in symmetrical acid anhydrides produce two bands.[13]

Experimental Section

Heneicosane-2,4-dione. Isomerization of Isopropenyl Stearate in the Presence of Diethyl Malonate.—Isopropenyl stearate (8.03 g), diethyl malonate (10.0 ml), and *p*-toluenesulfonic acid (100 mg) were heated to the reflux point, 185° pot temperature, using a short, inefficient reflux condenser so that acetone was not trapped and the high-boiling diethyl malonate was condensed and returned to the boiling pot. A second, efficient collection condenser trapped 0.88 g of acetone, identified as the 2,4-dinitrophenylhydrazone derivative. No acetone or other reaction product formed in significant amount in the absence of the acid catalyst. On cooling, the crude dione separated as orange impure crystals. Chromatography on a Florisil column, 4 × 50 cm, gave, on elution with pentane, a colorless solid residue containing the dione and some of the diethyl malonate. Trituration of the solid eluate cuts with ethanol gave the crude dione free of liquid ester. The colorless product recrystallized from pentane melted at 70 and 75° (double melting point): $\lambda_{max}^{isooctane}$ 298 mμ (log ϵ 3.48). The dione was much less soluble in pentane than the chief contaminant, ethyl stearate (m.p. 35°). The yield of dione was 70%.

Anal. Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42. Found: C, 77.90; H, 11.98.

The β-diketone on reaction with hydrazine gave two noncarbonyl-containing compounds, mp 101 and 75°, showing NH absorption bands at 3300 cm^{-1}. Refluxing the diketone in aqueous alcoholic sodium hydroxide gave the cleavage products, stearic acid and a neutral ketone presumed to be methyl heptadecyl ketone.

Duplication of the above rearrangement experiment with the sole variation of substituting 10.0 ml of Nujol for the "inert" diethyl malonate gave no β-diketone after 20 min of 185° and inconsequential amounts of β-diketone and of stearone after heating 1 hr at 200°. In both of these latter cases a substance absorbing intensely at 1815 cm^{-1} and at about 1150 cm^{-1} was produced (stearoketene?).[13a] The characteristic 1030-cm^{-1} band of stearic anhydride was completely absent.

Stearone from Isopropenyl Stearate.—Isopropenyl stearate, 16.1 g, was heated with 100 mg of *p*-toluenesulfonic acid to 200° for 1 hr. Acetone was liberated, and on cooling crystallization of the melt occurred. Chromatography on Florisil gave 2.87 g of unidentified foreeluate with methylene chloride, and 14 g of stearone eluted with a mixture of benzene–methylene chloride (1:1) fortified with 10% of methanol. The stearone eluted formed rhombic scales, mp 89–90.0°, lit.[14] mp 88°, and had an identical infrared spectrum with that of an authentic specimen. It was converted to the oxime, mp 69.2–70.0°, lit.[15] mp 62–63° (amorphous) for confirmation.

Anal. Calcd for $C_{36}H_{71}NO$: C, 80.98; H, 13.40; N, 2.62. Found: C, 80.74; H, 13.74; N, 2.82.

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(12) K. Nakanishi, "Infrared Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, Table 8.

(13) N. O. V. Sonntag, J. R. Trowbridge, and I. J. Krems [*J. Am. Oil Chemists' Soc.*, **31**, 151 (1954)] showed for stearic anhydride $\bar{\nu}_{max}$ 1735 and 1780 cm^{-1}.

(13a) Note Added in Proof.—This supposition of ester pyrolysis to hexadecylketene appears to be correct and will be the subject of a subsequent paper. The purified substance, mp 75.5–76.3, absorbs at 1752, 1715, 1645, and 1579 cm^{-1} (liquid film) and 1765, 1720, and 1645 cm^{-1} (CS_2) but may be dimeric.

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